Investigation of Hybrid Ionic Liquid Surfactants for Chemical Enhanced Oil Recovery (CEOR)

by

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13862

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Petroleum)

SEPTEMBER 2014

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Petroleum Engineering Programme
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BACHELOR ENGINEERING (Hons)
(PETROLEUM)

Approved by,

_____

(Associate Professor Dr. Cecilia Devi Wilfred)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
SEPTEMBER 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the reference and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

_____

THIBANKUMAR A/L ANANTHAKRISHNAN

ACKNOWLEDGEMENT

First of all, I would like to thank GOD for His Blessing and giving me the strength to successfully complete my Final Year Project with ease for this whole semester at Universiti Teknologi PETRONAS (UTP). There were many individuals and parties in which without hesitation I can say that my project could not be completed successfully without their generous assistance.

Special thanks to my supervisor, Associate Professor Dr. Cecilia Devi Wilfred. The supervision, support, encouragement and advises that she gave truly help the progression and smoothness of the project. This report could not also been completed without generous assistance from many sources. Over the months, the department of PETRONAS Ionic Liquid Center (PILC) has supplied necessary research facilities and technical guidance to me, and. I wish to thank all the (PILC) staff and graduate assistants and also the technicians of UTP Petroleum Engineering Department who directly or indirectly helped me in completing this project. in sincere, if inadequate, recognition of her long-standing support.

Last but not least, I would like to thank my family and friends for their moral support throughout the project as well as giving valuable tips and ideas which have guided me into completing this report successfully project.

ABSTRACT

Enhanced oil recovery (EOR) is being vastly applied and studied in the oil industry and various technologies have emerged over the last decades in order to optimize oil recovery after primary and secondary recovery methods have been applied.

Surfactant flooding is a chemical EOR method of injecting one or more liquid chemicals and surfactants into the reservoir for tertiary recovery in which the phase behavior of the reservoir can be manipulated by the injection of surfactants and co-surfactants, creating advantageous conditions in order to mobilize trapped oil. An excellent surfactant system can create micro-emulsions at the interface between water and crude oil, thus reducing the interfacial tension (IFT) which consequently will mobilize the residual oil and result in improved oil recovery.

Ionic liquids (ILs) are salts that are in liquid state below 100°C, composed wholly of anions and cations. Over the past decade, ILs has become one of the fastest growing 'green' media for chemists and engineers due to their superbly versatile physicochemical properties. Studies have shown that long alkyl chain ionic liquids have the potential to decrease the interfacial tension (IFT) of *n*-alkanes. The application of Hybrid ILs as a chemical EOR agent has a great potential in lowering the IFT against crude oil whilst being able to withstand harsh conditions in reservoirs such as high temperature and highly saline environment, thus giving good recovery factor of the stock tank oil originally in place (STOOIP).

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CHAPTER 1

INTRODUCTION

1.1 Background of the Project

Crude oil makes a major contribution to the world economy today. The provision of heat, light, and transportation depends on oil and there has not been yet a single energy source to replace crude oil that is widely integrated. By nature crude oil is a limited resource. In the phase of declining oil fields & at time when recovery of hydrocarbon is becoming more difficult, effective techniques are key to produce more oil from mature fields. Nevertheless, like a chain reaction, the ever increasing demand for hydrocarbons will result in the increase of its selling price and will therefore continue to increase if a secondary plan is not in place. This hard reality had then propelled the necessary drive to initiate oil & gas industry experts to widen the search for effective and practical techniques to maximize enhanced oil recovery (Thomas, 2008).

Approximately 65% of the crude oil remains trapped in an average oil reservoir after primary and secondary recovery (Rosen et al., 2005). Tertiary oil recovery or referred to as EOR along with stabilized oil production emerged as the field of study which interested many researches as producing residual oil entrapped within formation pores by mainstream method was not a possibility. Studies on chemical methods for Enhanced Oil Recovery (CEOR) had started way back since the 1960's. At that time, one of the proposed methods was using surfactant-based EOR. Surfactant- based EOR has been applied since the early 1970's and 1980's (Wu, et. al, 2009).

Surfactant is an abbreviation for surface active agents, which are polymeric molecules that lower the interfacial tension (IFT) between the liquid surfactant solution and the residual oil. Surfactants are also referred to as amphiphile molecules because they contain a polar or ionic water-soluble group attached to a non-polar insoluble hydrocarbon 'tail' chain within the same molecule, (Green and Willhite, 1998). Surfactants are generally categorized on the basis of their ionic nature of the head group.

The ionic nature of the head group namely;

(i) Anionic
(ii) Cationic
(iii) Non-ionic

are widely used in grouping of the surfactants whereby as the name suggest each possess a different characteristic which heavily depends on the quantity of aqueous solution that has been ionized by the surfactant molecules. Anionic surfactants have negatively charged head group, cationic surfactants consists of positively charged head group and non-ionic surfactants have no charged head group.

Surfactant flooding is one of the most efficient methods, but is also one of the most costly to implement. It is an EOR method of injecting one or more liquid chemicals and surfactants into the reservoir for tertiary recovery. The properties of the phase behavior in the oil reservoir are effectively controlled by this injection which mobilizes the trapped crude oil by lowering IFT between the injected liquid and the oil creating advantageous conditions that improves the oil recovery efficiency by lowering the capillary forces.

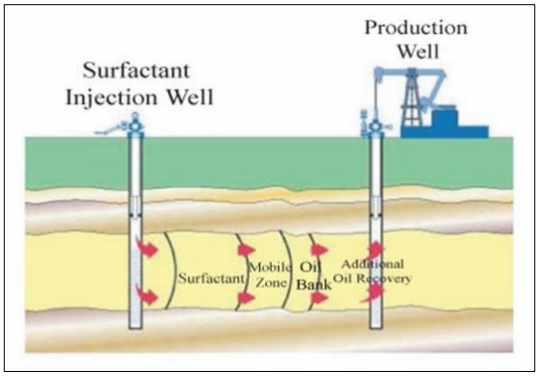


Figure 1: Surfactant flooding Enhanced Oil Recovery

1.2 Problem Statement

Various types of surfactants have been extensively used in the oil and gas industries as one of the methods for Chemical Enhanced Oil Recovery (CEOR). Many researchers have focused on this study and came out with ideas to generate and modify these surfactants. However, the problem is to find a suitable surfactant that is excellent in recovering oil at various conditions and also cost effective. Recent researches have proven that Ionic Liquid Surfactants are excellent in enhanced oil recovery. Hence, this research aims to investigate on hybrid ionic liquid surfactants for chemical enhanced oil recovery.

1.3 Objectives of the Project

The objectives of this project research are:

i) To study the physical and chemical properties of the synthesized ionic liquids [HMIM][DOSS].

ii) To produce a low IFT between the ionic liquid surfactant solution and the crude oil.

1.4 Scope of Study

The scope of study for this project will cover the following:

1. Synthesis of [HMIM][DOSS] ILs.

2. Study of synthesized [HMIM][DOSS] ILs characteristics with comprises:

   i. Thermogravimetry analysis (TGA)

   ii. Ion Chromatography (IC) analysis

   iii. Nuclear Magnetic Resonance (NMR) analysis

3. Investigation on EOR applications using Hybrid ionic liquid for Dulang and Baronia crude oils (IFT using the pendent drop method).

1.5 Relevancy of Study

This project will contribute to a huge significance to the oil and gas industry since many oil operators are focusing on the enhanced oil recovery development especially in Malaysia. At the end of this study, we are able to identify ILs capability as alternative approach agents in EOR, without overlooking the EOR's main purpose to recover high percentage of crude oil in reservoir.

1.6 Feasibility of Study

The following objectives listed are achievable and feasible within the given time frame. Before finalizing this project, all the parameters to be measured were clearly drafted and checked. Since 90% of the equipment and consumables to be used are available in UTP, there would be least chances of delay in the experimentation work. The IFT measurements are expected to complete within two to three weeks of the total project duration.

CHAPTER 2

LITERATURE REVIEW

2.1 Enhanced Oil Recovery (EOR)

The stage followed upon secondary oil recovery is known as Enhanced Oil Recovery (EOR) in which these technology functions to recuperate additions of ultimate oil that can be economically recovered from a petroleum reservoir, in excess of that which can be economically recovered by conventional primary and secondary methods (R.J. Watts, 1989). Also termed as tertiary recovery, EOR functions to restore formation pressure in addition develop fluid flow in the reservoir (Schlumberger) via three different techniques namely:

(a) Thermal recovery: Application of heat for oil thinning to ease extraction process. E.g. Steam flood and in-situ combustion.

(b) Gas displacement : Recovery of low-viscosity light crude oil (>20° API gravity) through the usage of miscible floods and/or immiscible floods utilizing gaseous compounds such as carbon dioxide, nitrogen and/or hydrocarbons as solvents.

(c) Chemical flooding: Usage of polymers or surfactants to ameliorate oil flow. One the most efficient but costly method to be implemented. The main workout of this method is to decrease the IFT between injection slug and crude oil. In mobilizing the residual oil, reducing the capillary forces by reducing IFT against crude oil can achieve significant fluid flow performance.

2.2 Surfactants

Schecther (1992) mentioned that surfactants are almost in every situation will be injected into hydrocarbon bearing reservoir apart from its applicability in all phase of well treatment whereby surfactants functions to;

- stabilize oil and water emulsion, or, on contrary, break undesirable emulsion.
- alter wettability.
- increase solubility of oil in water.

The existence of a hydrophilic head group and a hydrophobic chain (or tail) as the basis in the molecule of the aqueous surfactant solutions serves as its key distinctive property. Schramm (2000) explained that the polar or ionic head group normally interacts with an aqueous condition, in which case it is solvated via dipole-dipole interactions. Therefore, in EOR surfactant flooding applications the interaction between the hydrophilic head with water molecules and the hydrophobic tail interacts with the residual oil in which a water-in-oil or oil-in-water emulsions is formed. (Pashely and Karaman,2004).

Another term that needs to be paid attention would be the surface flooding injection, in which it is a method whereby one or more liquid chemicals and surfactants are injected that efficiently controls the phase behavior properties in the oil reservoir. This results in the reduction of IFT between the injected liquid and the oil via mobilization of the trapped crude oil (Sandersen, 2012). In other words, surfactants are added to decrease the IFT between oil and water.

However, the efficiency of the of surfactant to reduce IFT between oil and water however may be influenced or prohibited by certain physical reservoir characteristics such as adsorption to the rock and trapping of the fluid in the pore structure that would result in the significant losses of the surfactant. Therefore, it is vital to be aware of such high losses of surfactants that occur as a result of adsorption and phase partitioning inside the reservoir as the surfactants sensitivity to high temperatures and high salinity. With this, rations for

creating surfactant systems which can withstand such conditions or the other option will be to conduct further investigation.

The optimization criterion in surfactant flooding is to maximize the amount of oil recovery, while minimizing the chemical cost. While it is necessary to reach low IFT for the surfactant system, minimizing only the IFT may not always coincide with optimal oil recovery, as low IFT is not the only essential condition to meet in order to get a successful and efficient oil recovery (Fathi, 1984).

2.3 Ionic Liquids

Ionic liquids, ILs, are salts that are in liquid state below 100°C, wholly composed of cations and anions. Today, researches are developed to study the effectiveness of ILs as an EOR agent in flooding methods. Numerous studies prove that long alkyl chain ionic liquids are capable to lower the IFT of n-alkanes. With such, ILs have attracted much interest and gained acknowledgment as potential environmentally benign solvents due to some of their inimitable properties. These properties of ILs result from the composite properties of the wide variety of cations and anions. (Mustafizur Rahman, 2006)

Most of the ILs are liquid at room temperature and usually exhibit negligible vapor pressure, which reduces the possibility of air pollution and loss of materials at ambient conditions (John D. Holbrey, 2003). This is how ILs become one of the most popular „green" media for chemists and engineers due to their superbly versatile physicochemical properties (Divya Nair G, Development of Ionic Liquids as a Novel EOR Agent Master Symposium, 2012). They have been studied as novel solvents for organic synthesis polymerization, and liquid-liquid extraction, in electrochemical studies (Zhiying Li, 2004), gas chromatography (Daniel W. Armstrong), and for catalysis (Zhongkui Zhao, 2005).

One of the distinctive applications of ILs is as novel EOR agent, as has been shown in a few earlier publications. Taking into account of the miscellaneous challenges associated with diverse traditional EOR agent, ILs hold prospects as alternative in the rapidly growing EOR. The reasons of choosing ILs to be the research subject matter are due to its properties i.e. the aggregation number can be controlled by changing the length and shape of the hydrocarbon tail, the type of polar head group, and/or the nature and size of the counter-ion. In other words, varying the cationic and anionic components in ILs can change their physical and chemical properties in a systematic manner.

Accordingly, this promising ILs can serve as new EOR options with important advantage of being non-volatile liquid over a wide temperature range. ILs contains long alkyl chain of having hydrophilic imidazolium head group and hydrophobic tail. This unique characteristic allows ILs to act as a good option for surfactants.

2.4 Interfacial Tension (IFT)

Producing a low interfacial tension between water and crude oil are of specific concern in oil recovery. The physical phenomenon that arises between two immiscible liquids (oil and water) is termed interfacial tension (IFT) which results from the attractions due to intermolecular forces. In a bulk fluid, every molecule is surrounded by equivalent neighboring molecules resulting in the balance of intermolecular force to be zero. A molecule at the interface of immiscible liquid is surrounded with two different neighboring medium and creates an inward force. These molecules are subjected to a molecular attraction balanced by the fluid's resistance to compression. Thus, allowing the surface to act like a stretched elastic membrane. Several methods have been developed for IFT measurements; however the two popular methods used for researches are the pendent drop method and the spinning drop method.

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

1. • Title Selection
2. • Preliminary research on Chemical Enhanced Oil Recovery (CEOR), identification of various chemical surfactant used in CEOR and the problems faced during its usage on various conditions.
3. • Experimental Setup - Perform lab and equipment booking, purchasing of chemicals 1-methylimidazolium, 1-bromohexane, sodium dioctyl sulfosuccinate and ENORDET to conduct the experiments. Attend lab safety briefing and training on how to operate the IFT OCA 20 equipment.
4. • Experimental Work - Synthesizing of ionic liquid, testing on various physical and chemical properties of the ionic liquid and conducting experiments on IFT measurements using the hybrid ionic liquid surfactant at different concentrations with Dulang and Baronia crude oils.
5. • Analysis of Result - All the results were tabulated and analysed accordingly.
6. • Discussion of Result Analysis - All results were discussed and compared tothe literature review.
7. • Final Report and Presentation

Research and experiments will be conducted in three systematic sections:

1. Ionic liquids syntheses

2. Ionic liquids characterization

3. Investigation of EOR applications using Hybrid Ionic Liquid

3.2 Ionic Liquids Synthesis

Ionic liquids are generally synthesized by a quaternization reaction of amines, N-heterocycles, or phosphines with alkyl halides in an *SN2* type reaction similar to Figure 2. If another anion is desired than that formed in the quaternization step, an anion exchange can be performed with the corresponding acid or salt (Sylvia O. Nwosu, 2009).

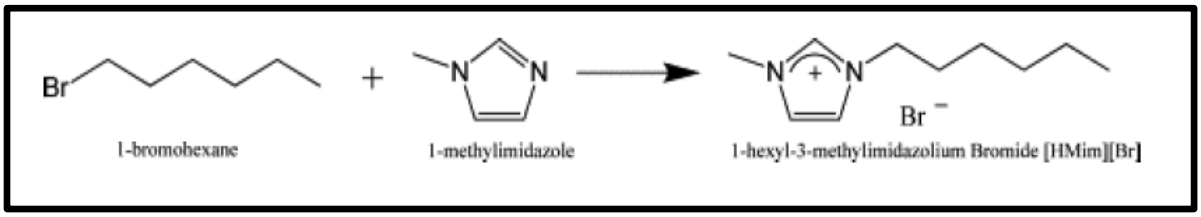


Figure 2: Synthesis of 1-hexyl-3-methylimidazolium bromide

Large solvent effects on the kinetic rate are observed with the qualitative trend that rate increases with increasing solvent "polarity". Reactions involving ionic liquid synthesis are highly exothermic, and require adequate heat removal or a solvent or both. A solvent is also useful as some ILs or their intermediates are actually higher melting-point solids or viscous liquids, which would require much different processing techniques.

The syntheses of ILs are segregated into two distinctive sections:

i. Quaternization

ii. Metathesis

3.2.1 Theoretical Calculation

Calculations are done before the experiment was conducted to ensure sufficient yield of more than 10g of ionic liquids is achievable. Basic equations to calculate mole, mass, volume and density are applied with a basic assumption of equimolar reaction of 1 to 1 mole.

3.2.2 Quaternization

These steps form the cation of the ionic liquid, the synthesis of 1-hexyl-3-methylimizazolium bromide.

1. A 100 ml 3-headed round-bottomed flask is flushed with dry nitrogen. The apparatus is set on the reflux heater and conducted in fume chamber.

2. The reflux heater is configured with thermocouple set up for temperature measurement and it is dipped inside the oil bath. A test run is done before starting the experiment.

3. A 12 ml syringe is used to charge methylimizadole into the 3-headed round bottomed flask at the rubber stopper.

4. Then, 1-bromohexane is added to the flask slowly using the 12 ml syringe. This is to avoid vigorous smoke release.

5. The solution is then heated under reflux and under nitrogen atmosphere at 70°C and 500 rpm for 72 hours. Nitrogen is set to flow at 10 cc/min air and 85 bar.

6. The magnet stirrer is observed and the speed is increased from 500 rpm to 800rpm gradually.

7. After 72 hours, the reflux heater is stopped and the solution is cooled down to room temperature.

8. Next, the solution is washed with 15ml of ethyl acetate for 3 times. The washing is done by shaking the mixture manually until the clear ethyl acetate solution turns cloudy.

9. Step 8 is repeated using 15 ml of diethyl ether.

10. Finally, the washed solution is dried in a vacuum line at 60°C for 72 hours.

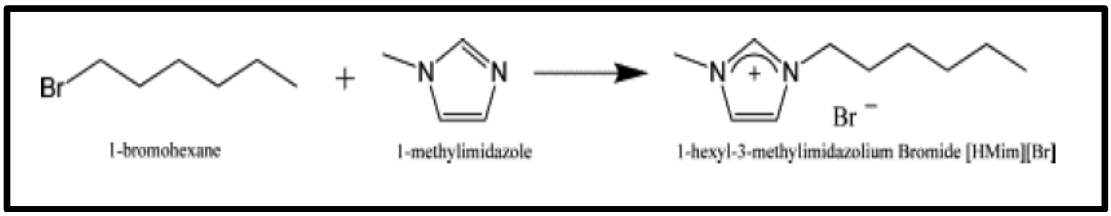


Figure 3: Quatenization of 1-hexyl-3-methylimidazolium bromide

3.2.3 Metathesis

Upon completion of the quaternization process, the [HMIM][Br] is metathesized into [HMIM][DOSS] with the following process:

1. 1-hexyl-3-methylimizazolium bromide is mixed in 50 ml of acetone using a 100ml Erlenmeyer flask and stirred with a magnetic stirrer until it dissolves completely.

2. An equimolar amount of sodium dioctylsulfosuccinate is handled in a similar manner as step 1.

3. Both the mixture are then combined and stirred at room temperature for 1 hour 30 minutes.

4. The solution is filtered using a filter paper and the solid precipitate (NaBr) is removed.

5. Next, the solution is heated using Rotary Evaporator at 50°C and pressure 500mPa to remove volatile solvent for 30 minutes.

6. The moisture from the compound is removed under vacuum line at 60°C for 24 hours.

7. Finally, the remaining solvent is removed under vacuum oven at 60°C for 48 hours to get [HMIM][DOSS].

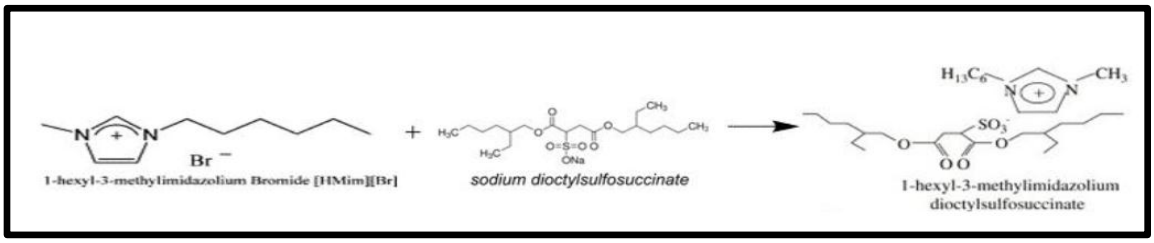


Figure 4: Metathesis of [HMIM][DOSS]

3.3 Ionic Liquids Characterization

Upon ionic liquid synthesis, detailed analysis and observations are required to further research on ionic liquids capability as an alternative EOR surfactant. In order to study the chemical and physical properties of ionic liquid a few tests is conducted as below:

i. **Water Content -** to examine the amount of water in the synthesized ionic liquid

ii. **Thermogravimetry Analysis -** to measure the temperature the ionic liquid decompose

iii. **Viscosity & Density Measurements -** to analyze the viscosity and density of the ionic liquid

iv. **NMR Analysis -** to confirm the structure of the synthesized ionic liquid

3.4 Investigation for EOR Applications using Hybrid Ionic Liquid

The ionic liquid synthesized is tested against Dulang and Baronia crude oil for IFT. Concentrations ranging from 0.2% -1.0% will be tested to determine the optimum IFT. Based on the IFT results, 3 different series (A series, O series and J series) comprising of 6 commercial surfactants at a range of 0.2% - 1.0% concentration will be added to the optimum ionic liquid concentration to further test the reduction of IFT.

3.4.2 IFT Measurements

Pendent Drop Method

1. Clean the capillary nozzle of the IFT OCA 20 using compressed air.
2. Fill the cell through the glass tube with different concentrations of ionic liquid surfactants.
3. Release a drop of crude oil through the capillary nozzle into the cell.
4. Adjust the camera focus to get a sharp image of the drop.
5. The geometry of the drop is analyzed optically and the IFT is measured.
6. The obtained results are tabulated

3.5 Equipment and Tools

In this project, the main equipment used is the IFT OCA 20 manufactured by DataPhysics. This equipment helps to measure the IFT of the surfactant and crude oil at reservoir conditions using the pendent drop method.

The IFT OCA 20 has many operating and handling benefits such as it can measure the interfacial tension ranging up to 2×10^{-3} mN/m, and it can operate at temperature range of ambient to 175^{o}C.

Besides that, the IFT OCA20 is easy to use and has a low maintenance cost since most of the parts are stainless steel. On the other hand, the IFT OCA 20 also gives a very good stability to the drop allowing it to be easily analyzed.

Figure 5 shows the schematic and the actual DataPhysics IFT OCA 20 equipment used.

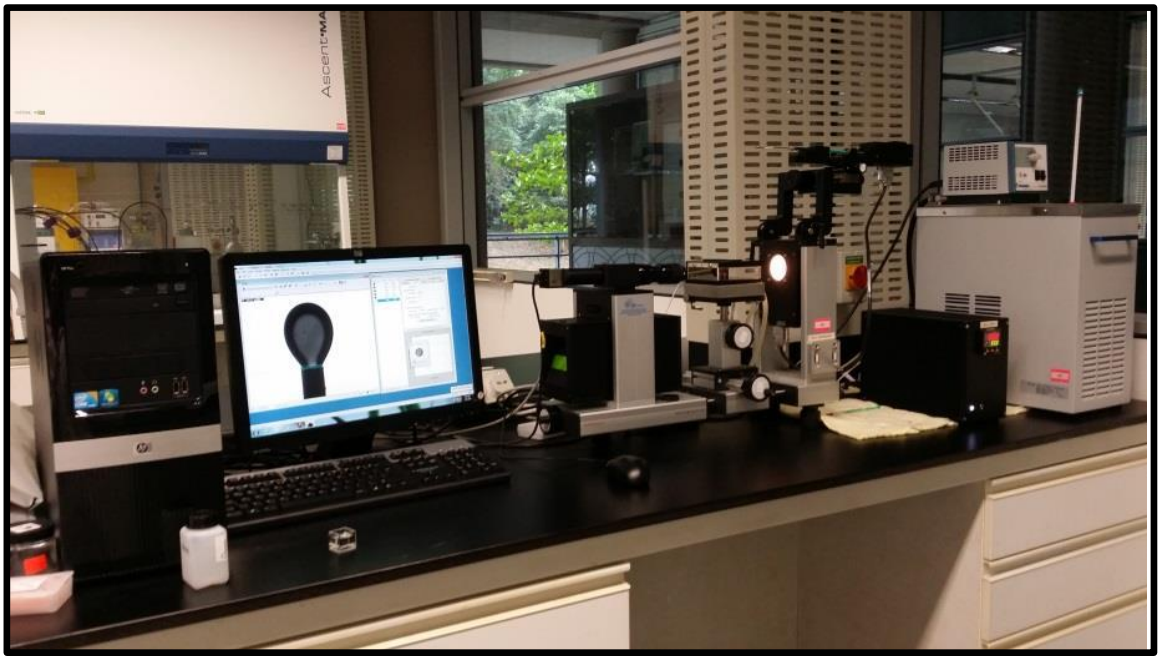
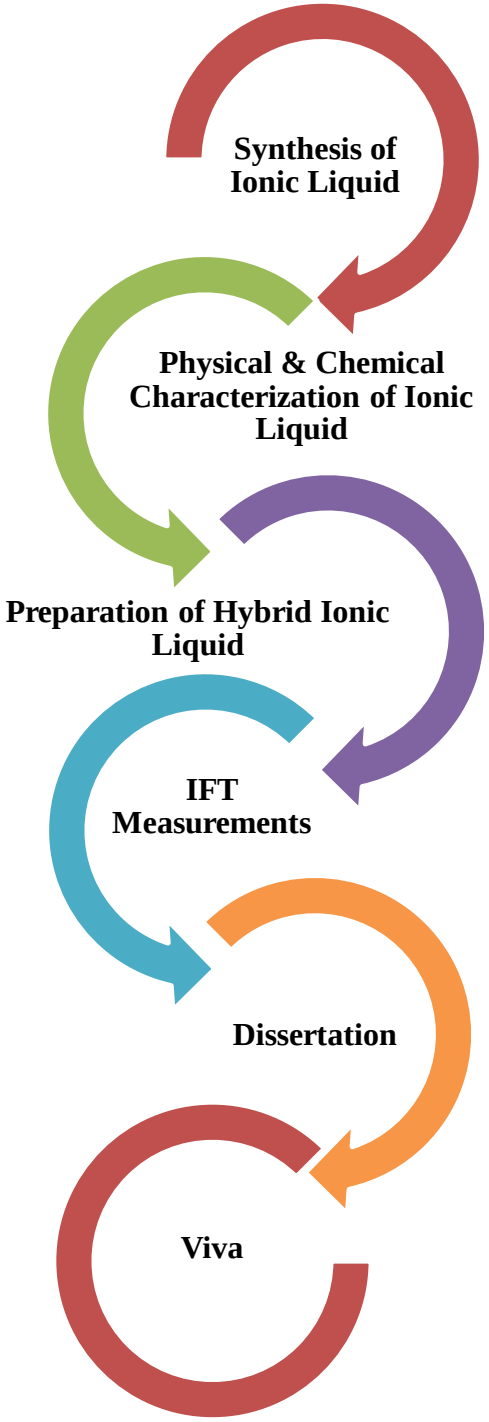


Figure 5: The IFT OCA 20 Pendent Drop Equipment

Other equipments used in this experiment are reflux heater, rotary evaporator, vacuum oven, beaker, measuring cylinder, digital weighing machine, heater-mixer, etc.

3.6 Key Milestone

There are a few key milestones to be achieved in this project. The key milestones are as follows:-



3.7 Gantt Chart

Final Year Project (FYP 1)

No	Description	Weeks													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of project title														
2	Preliminary research study														
3	Submission of Extended Proposal							★							
4	Proposal Defense								★						
5	Further literature review & methodology study														
6	Interim report preparation														
7	Submission of draft Interim report													★	
8	Submission of Interim report														★

Final Year Project (FYP 2)

No	Description	Weeks													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Synthesis of Ionic Liquid														
2	Physical & Chemical Characterization of Ionic Liquid														
3	Submission of Progress Report							★							
4	IFT (Pendent Drop) Experiment														
5	Pre-Sedex presentation									★					
6	Sedex presentation										★				
7	Submission of draft final report											★			
8	Submission of dissertation (softcopy)												★		
9	Submission of technical report												★		
10	Viva													★	
11	Submission of dissertation (hardcopy)														★

Process

Dateline

CHAPTER 4

RESULTS & DISCUSSION

4.1 Properties of the Crude Oil

Table 1: Crude Oil properties

Crude	API	Type	SG@60℃	Total Acid Number
DULANG	37.8	Light	0.8358	0.37 mgKOH/g
BARONIA	29.79	Medium	0.8773	0.24 mgKOH/g

4.2 [HMIM][DOSS] Synthesis

4.2.1 Calculation

Table 2: Quaternization Process Data

Chemical	**MW (g/mol)**	**Density (g/cm^3)**	**Boiling Point (^oC)**	**Amount (moles)**	**Volume (ml)**	**Mass (g)**
1-Methylimidazole	82.10	1.030	198	0.1	7.97	8.21
1-Bromohexane	165.07	1.276	154	0.15	19.40	24.76

The quaternization process calculation in Table 2 is based on the assumption that the reaction is equimolar with an excess of 0.05 moles of 1-bromohexane, taking 1-methylimidazole as the limiting reagent. The equations used are:

$$\rho = M/V$$

$$\text{mole} = m/MW = \rho\ V / MW$$

Where,

ρ = density g/cm3

m = mass, g

V = volume, mL

MW = molecular weight

4.2.2 Observation & Discussion

Before starting the synthesis, the thermocouple sensor is checked to ensure it is at all-time dipped into the oil bath, so that the temperature measured reflects the correct value shown on the hot plate. If this is not done correctly, the heating process of the oil bath will not stop, and this will eventually cause fire. Figure 6 below shows the synthesis of [HMIM][Br].

Figure 6: Synthesis of [HMIM][Br]

While mixing 1-methylimidazole with 1-bromohexane, 1-bromohexane is slowly added into the flask drop by drop to avoid vigorous smoke as the reaction is exothermic. The 3-headed round bottomed flask with the 1-methylimidazole solution has to be fully submerged into the oil. This is to ensure the constant temperature distribution throughout the synthesis. The stirring speed is increased gradually as more force is needed to stir the solution when the reaction creates a more viscous solution.

In the beginning, an excess of 0.05 mole of 1-bromohexane is being used to carry out the study, while 1-methylimidazole is acting as the limiting reagent. The reason is to ensure that all of the 1-methlylimidazole is completely reacted. The quaternization process takes three days to complete.

The study is carried out using a reflux heater to heat the reactants while continually cooling the vapour to be returned back to the flask as liquid. The reaction is also carried out under the presence of nitrogen gas to ensure that the air is inert and no loss of solvent occurs through constant evaporation.

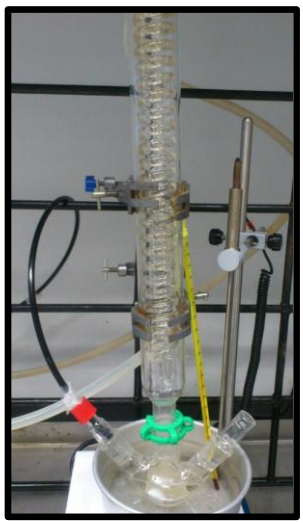


Figure 7: Reflux heater

Initially, both 1-methylimidazole and 1-bromohexane are colourless. Upon quaternization process, a viscous colourless liquid is formed. In order to know if the quaternization process is completed, a Thin Layer Chromatography (TLC) is carried out.

Thin Layer Chromatography

Thin layer chromatography, TLC, is among the most useful tools for following the progress of organic chemical reactions.

TLC is performed on a sheet of plastic, coated with a thin layer of adsorbent material, which is also known as the stationary phase. The product sample is deposited as a spot on the stationary phase. At the same time, another spot of reactant of sample is deposited on the same level, in this study, it is 1-methylimidazole. The bottom edge of the plate is placed in a solvent mixture of 7ml Acetone and 3 ml Methanol, which its function is to move up the plate by capillary action. As soon as the solvent reaches to almost the other top edge, the plate is removed from the solvent and let to dry.

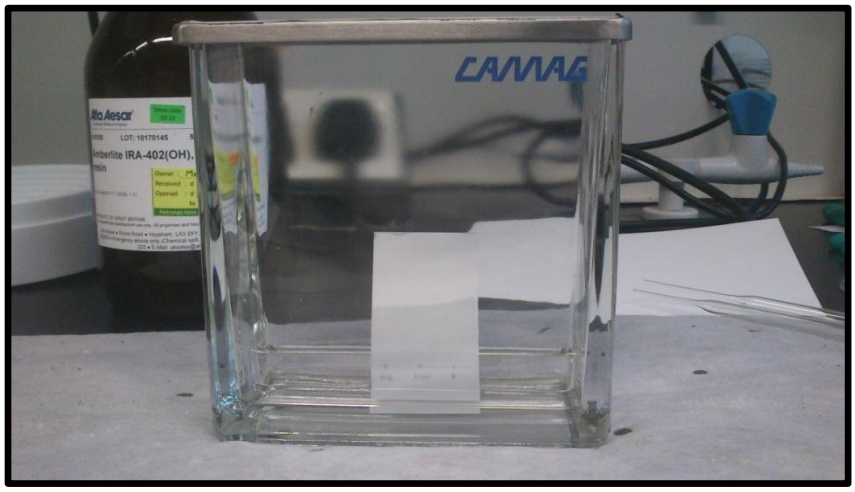


Figure 8: Thin layer chromatography (TLC)

Two spots are being observed at two different levels on the plate. If the product spot is lower that the reactant, it indicates that the quaternization reaction is completed. Since these spots usually fade, it is a good idea to circle the spots with a pencil while they are still visible in order to have a permanent record of the chromatogram. This can be shown in Figure 9 below.

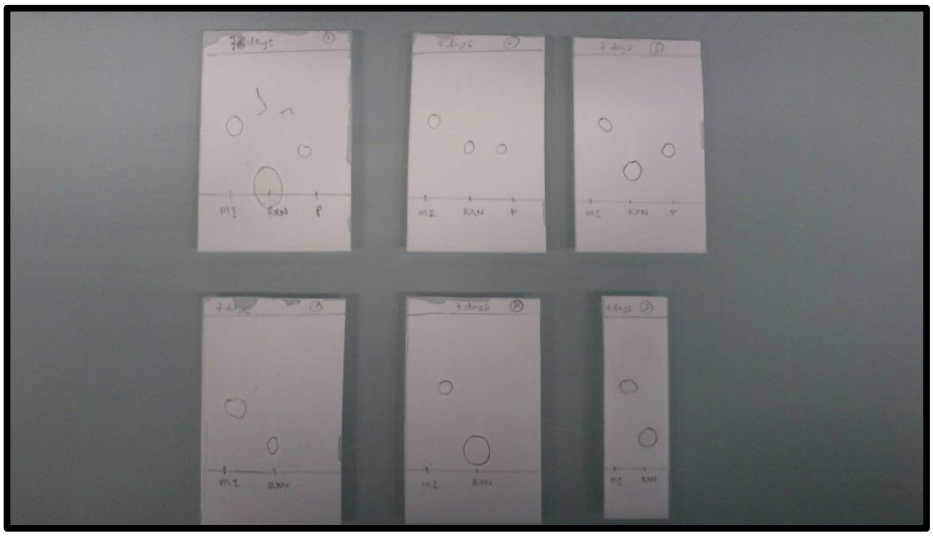


Figure 9: TLC plates analysis

Washing the products after the reaction is essential to get rid of the access reactants. The products turn from colourless to cloudy after washing. If there is any access reactant, two layers of liquid is formed. The mixture will not mix due to the different densities of the products and the solvent. However, only one layer of solution is being observed after the washing. The possible reason is that all the reactants have been completely reacted, leaving no access reactants.

Figure 10: Washing of [HMIM][Br]

As shown in Figure 10, the picture on the left shows the physical properties of the solution before washing, and the picture on the right shows the appearance of the solution after washing.

The product is the placed in the Rotary Evaporator to remove the solvent. The chemical is found to be more viscous and colourless after taken out from Rotary Evaporator, as the volatile solvent has been removed. Finally, the remaining solvent is removed under vacuum oven for 48 hours to get [HMIM][Br].

After vacuum oven, most of the remaining solvent is being removed. This is the explanation of the change in colour of the chemical from colourless white into yellowish liquid. Apparently, besides the colour, the chemical appears to be more viscous.

A purification process is conducted to remove any impurities left in the ionic liquid after the quaternization process. Equal amounts of ionic liquid are dissolved into Methanol and 1/10 of activated charcoal which is let to stir for 3-4 hours in a single round bottom flask. Activated charcoal is known to be a good absorbent. Thus, it removes any excess impurities in the ionic liquid and also decolourizes it in the case of excess heating. The Figure 11 below shows the [HMIM][Br] before and after purification. To confirm the structure of the products, the sample is sent for NMR analysis.

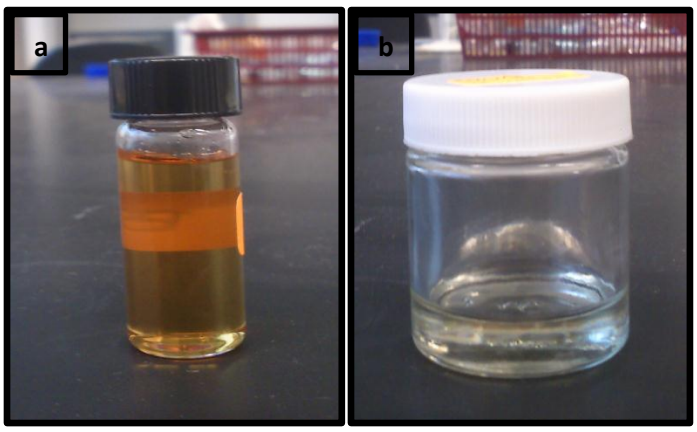


Figure 11: (a) Before purification (b) After purification

Metathesis of [HMIM][Br] and [Na][DOSS] is conducted at room temperature for 1 hour 30 minutes. Initially, both the components are mixed separately in acetone as an intermediate solvent. It is essential to use solvent to mix with [Na][DOSS] because it is in solid state in room temperature.

Due to the high volatility of acetone, the flask has to be closed when carrying out the mixing of the chemical solution. This is to avoid the loss of the sample. The reactions are equimolar. Filter paper is being used to remove the solid precipitate as the reaction produces solid precipitation. The white solid precipitate is NaBr with no odour. This can be seen in Figure 12, the solid precipitate, NaBr.

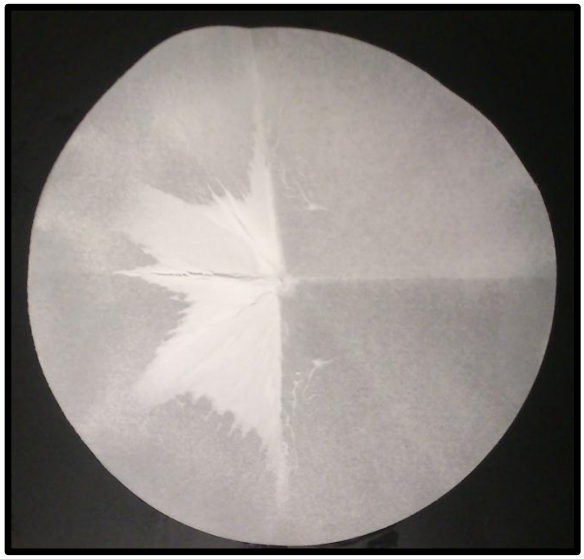
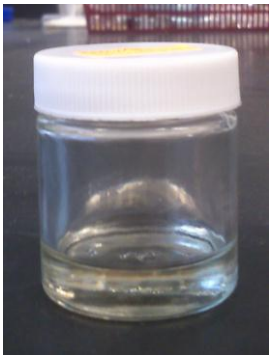


Figure 12: Solid precipitate, NaBr

The purified product is placed in the Rotary Evaporator. A temperature of 50°C is set for water bath and a pressure of 500mPa is set to remove the solvent acetone as the boiling point of the solvent is 56°C. The process takes about 180 minutes to complete before proceeding to the vacuum oven. The products are dried under the vacuum oven for 72 hours at 60°C.

Table 3: Final synthesis product

Chemical	Sample	Colour	Physical State	Yield, g (%)
[HMIM][Br]		Transparent	Viscous	14.000 (95%)
[HMIM][DOSS]		Light Yellow	Viscous	22.000 (92%)

4.3 Characterization of [HMIM][DOSS]

Water Content

Table 4: Water Content of [HMIM][DOSS]

Ionic Liquid	Water Content, ppm			
[HMIM][DOSS]	Trial 1	Trial 2	Trial 3	Average
	1894.322	1900.112	1900.215	1898.216

Generally, most ionic liquids are desired to have water content between 100 ppm to 1000 ppm. However, based on the experiment conducted it shows that the synthesized [HMIM][DOSS] still contains a high amount of water which needs to be removed. This might be due to the unavailability of the vacuum line to effectively remove water from the sample.

Figure 13: Karl Fisher Titration

Nuclear Magnetic Resonance (NMR) Analysis

Based on the NMR results obtain in Figure 14 and Figure 15, it can be confirmed that the synthesis of [HMIM][DOSS] is done correctly. The number of proton obtained from the NMR test tallies with the structure of the sample. Table 5 summarizes the proton NMR results for both [HMIM][Br] and [HMIM][DOSS].

Table 5: NMR Analysis of [HMIM][Br] & [HMIM][DOSS]

Sample	NMR
[HMIM][Br]	0.826 (3H), 1.237 (6H), 1.773 (2H), 3.888 (3H), 4.203 (2H), 7.803 (1H), 7.887 (1H), 9.400 (1H)
[HMIM][DOSS]	0.871 (15H), 2.423 (22H), 1.510 (2H), 1.784 (2H), 2.823 (1H), 2.917 (1H), 3.860 (7H), 4.165 (2H), 7.784 (2H), 9.137 (1H)

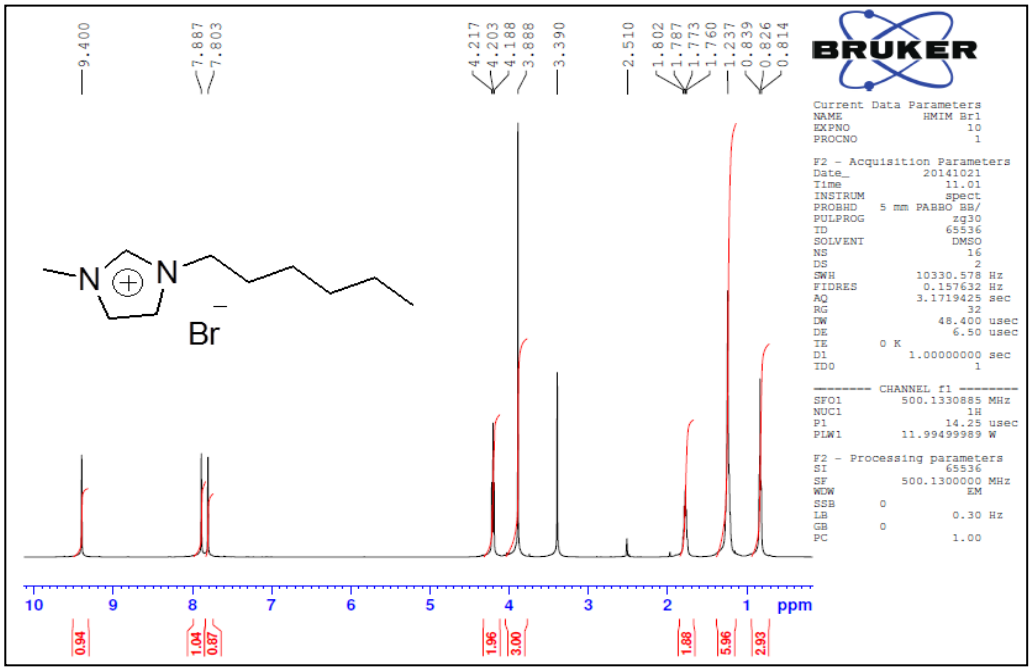


Figure 14: NMR [HMIM][Br]

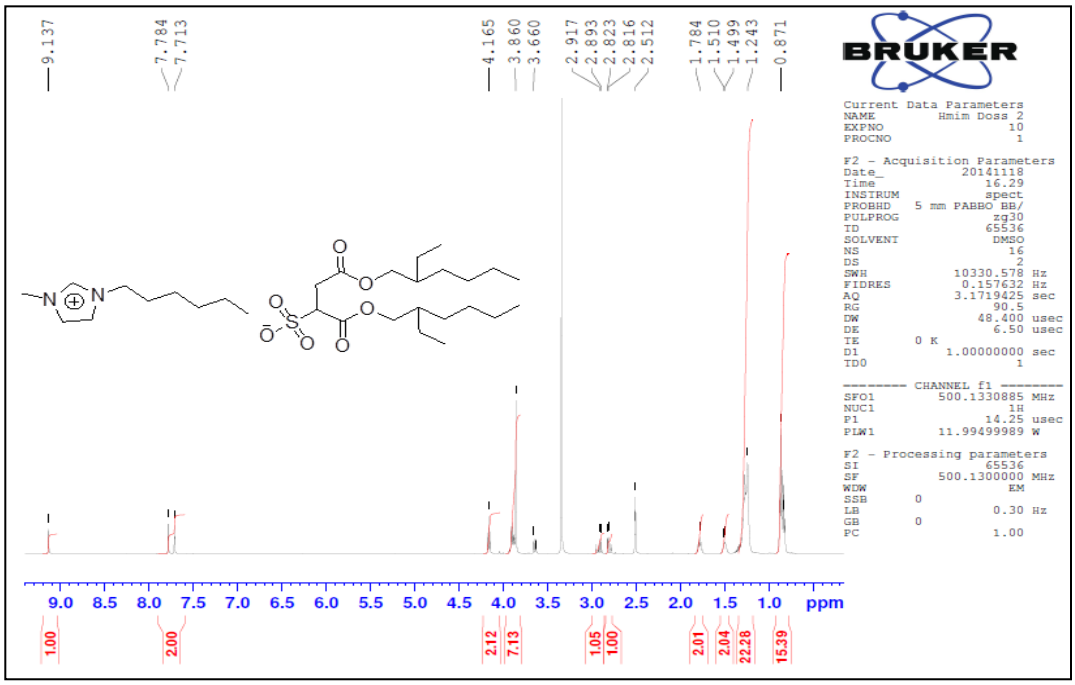


Figure 15: NMR [HMIM][DOSS]

Ion Chromatography (IC) Analysis

Ion Chromatography is done to check on the halide content in this case bromide which is still present in the synthesized [HMIM][DOSS] IL. Theoretically, the halide content present should be lower than 10 000 ppm (< 1%). However, from the IC results obtained it shows bromide content of 41 000ppm (4.1%). This clearly shows that [HMIM][DOSS] is not 100% pure and there are still presents of some starting material. This might be due to insufficient washing of the synthesized [HMIM][DOSS] to cause some of the bromide to be trapped within the IL. Figure 16 shows the overlay curves and concentrations of bromide in [HMIM][DOSS].

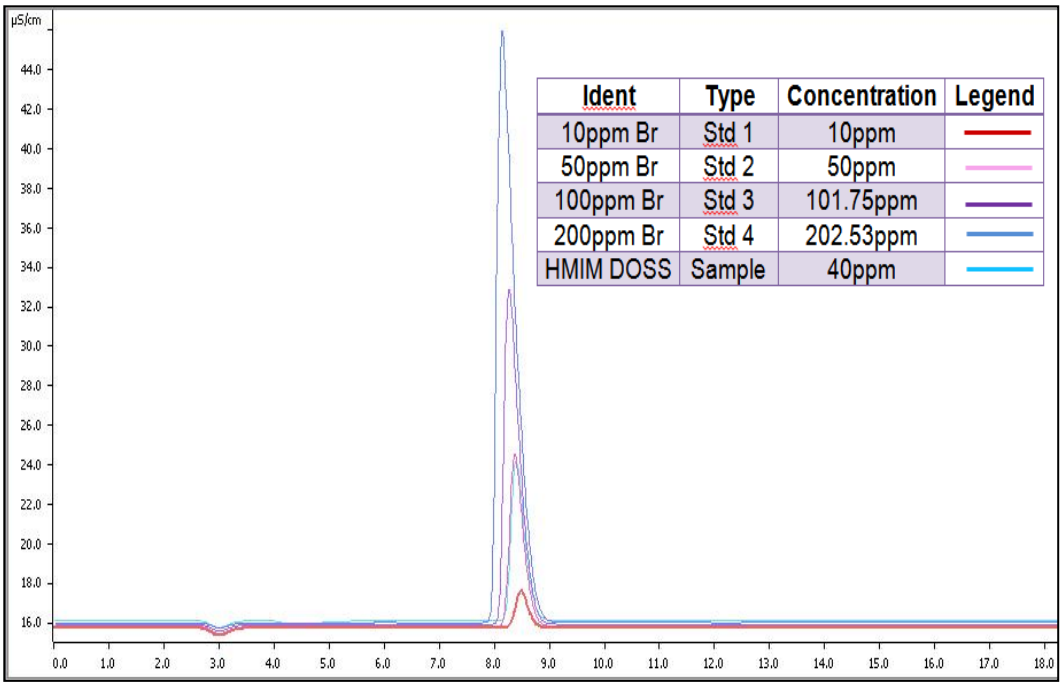


Figure 16: Ion Chromatography Overlay for 1000 ppm [HMIM][DOSS]

Thermogravimetry Analysis (TGA)

The thermogravimetry analysis (TGA) is performed to check the decomposition temperature and thermal stability of [HMIM][DOSS]. Based on the experiment performed, we can observe the changes in weight with respect to changes in temperature. The TGA analysis in Figure 17 shows that [HMIM][DOSS] starts to decompose at 262.23°C and with complete decomposition at 350°C. This shows that the synthesized [HMIM][DOSS] has a high thermal stability.

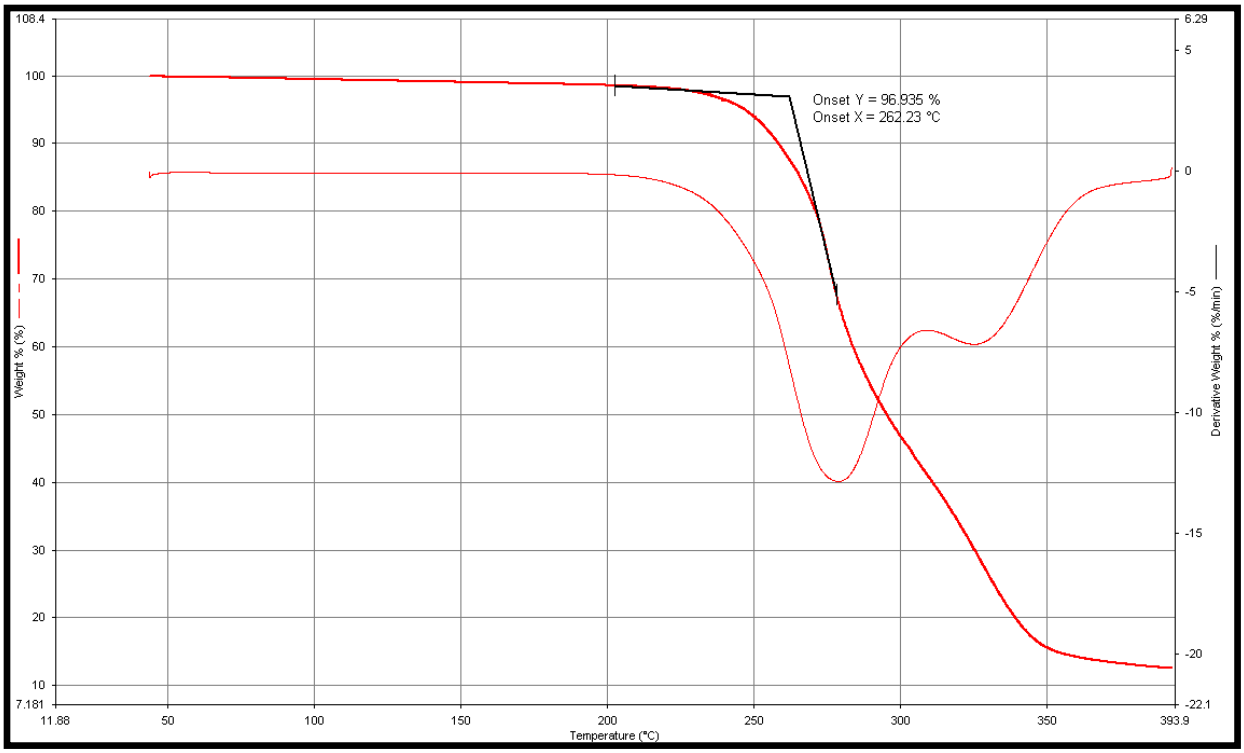


Figure 17: Thermogravimetry analysis (TGA)

4.4 IFT Experiment

There are several factors which affect the IFT behavior such as concentration, temperature and salinity. For this project, only the surfactant concentration is varied from 0.2% to 1.0% while the other parameters such as temperature and salinity are kept constant at 60°C and 20 000ppm. The hybrid IL surfactants were measured with Dulang and Baronia crude oil.

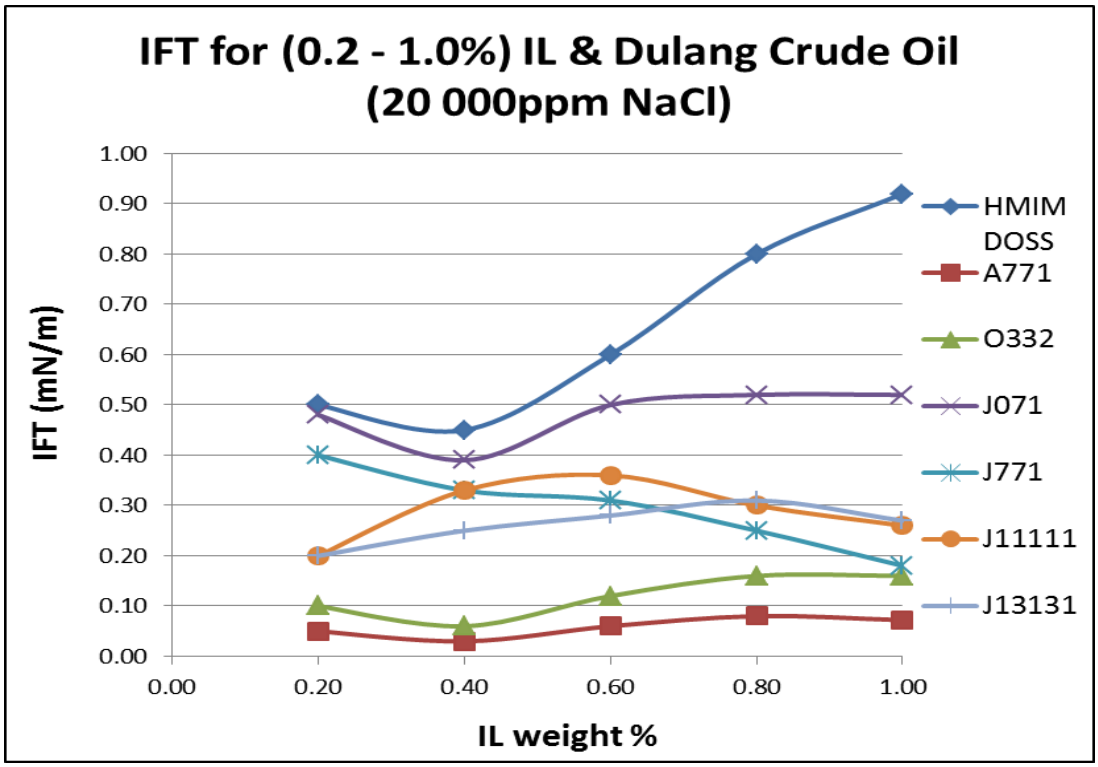


Figure 18: IFT of Hybrid IL with Dulang Crude Oil

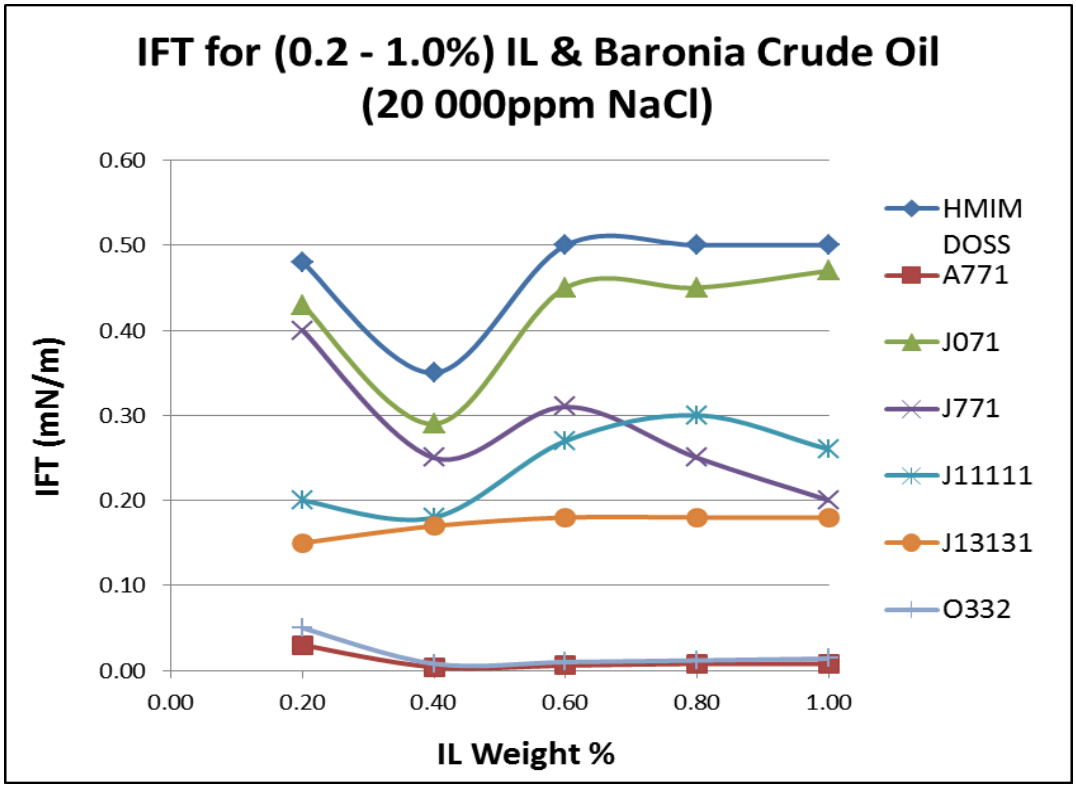


Figure 19: IFT of Hybrid IL with Baronia Crude Oil

From Figure 18 and Figure 19, it shows that [HMIM][DOSS] gives a low IFT at concentration of 0.4% for both Dulang and Baronia. This same trend is also obtained for the A771 and O332 hybrid IL surfactant. This turning point is known as the Critical Micelle Concentration (CMC). It is most important to determine the desired surfactant concentration blend to be injected in order to achieve a low IFT.

Furthermore, the reason which causes the reduction of IFT with increasing surfactant concentration is because surface tension decreases sharply since there is an excess concentration of surfactant molecules at the interface, it increases the mixing ability of the two liquid thus lowers the interfacial tension between them. So it is easier to stretch the surface of the interface. However, when they start saturating the system, the surfactant dissolution in system changes, reverse the distribution coefficient thus change fluid-fluid interaction and reverse the effect. Therefore, determination of CMC point for each type of surfactant is important since CMC known to be the economical concentration for surfactant flooding. Economic perspective of surfactant injection is very important which optimum injection design is needed.

Besides that, the IFT value for hybrid IL is lower with Baronia crude oil as compared to Dulang crude oil. This is because the TAN for Dulang is higher compared to Baronia. In the case of high total acid number (TAN) crude oils, alkaline is often added with the surfactants. Alkaline generates additional soaps through reaction with naturally occurring acids in the crude oil which further reduces the IFT.

4.5 Cost Evaluation

Table 6: Price of chemicals

Chemicals	Price per bottle	Price per gram
1-Bromohexane	$15.00 (100 gram)	$0.15
Dioctyl Sulfosuccinate, Sodium Salt	$35.10 (100 gram)	$0.35
1-Methylimidazole	$23.50 (100 gram)	$0.24

Table 7: Price for chemicals used to produced 22.000 gram of [HMIM][DOSS]

Chemical	Chemical Price
1-Bromohexane	**$ 0.75 (5 grams)**
Dioctyl Sulfosuccinate, Sodium Salt	**$ 6.30 (18 grams)**
1-Methylimidazole	**$ 2.88 (12 grams)**
Total	**$ 9.93**

By comparing the price of the synthesized Hybrid IL to the available commercial surfactant being used, the following research can be found. Depending upon the field properties, type of surfactant and water salinity, a typical 0.2% - 1.0% commercial surfactant will cost between $2.30 and $3.50 per barrel injected while the cost of synthesized Hybrid IL will be approximately $1.00 - $1.90 per barrel injected. This shows that Hybrid IL's are cost effective to be used in the oil field.

CHAPTER 5

CONCLUSION & RECOMMENDATIONS

5.1 Conclusion

Based on the findings and results illustrated in this study, it can be concluded that hybrid ionic liquids has a great potential to be used as a surfactant for chemical enhanced oil recovery. On the basis of the results obtained, Hybrid IL's are very versatile and could be tailored to suit specific processes. The hybrid ionic liquid synthesized in this project was tailor made to have a hydrophobic and hydrophilic property so that it could be used as a surfactant. The superbly versatile physicochemical properties, non-volatile, non-flammability and high thermal stability makes ionic liquid be classified as a "Smart Liquid" since no molecular solvent, except perhaps some liquid polymers, can match the liquidus range of ionic liquids or molten salts. A thermal stability of 262.23℃ was obtained from the synthesized ionic liquid surfactant making it suitable to be used in reservoir conditions below 200°C.

Besides that, the hybrid IL has a high tendency to further reduce the IFT. The results obtained shows excellent IFT reduction when using A771 & O332 Hybrid IL with both Dulang & Baronia crude oil. By reducing the IFT, the residual oil saturation increases, thus increasing the efficiency of the oil recovery.

Moreover, the Hybrid IL's are also cost effective to be used even during the drop of oil prices. These experimental results show the potential of the new Hybrid IL surfactant system as a promising chemical flooding formulation for most Malaysian reservoirs.

5.2 Recommendations

There are a few recommendations can be listed to enhance the study in future. ILs synthesized should always be kept in the desiccators. This is to avoid atmosphere moisture from altering the chemical properties. Besides that, the synthesis of ILs should be done patiently in order to achieve a pure ionic liquid and also extra amount should be prepared for further tests. On the other hand, further studies such as surfactant adsorption to the rock, core flooding, sweep efficiency studies and corrosion analysis of the hybrid ILs should be done in order to better understand the surfactant for chemical enhanced oil recovery usage.

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